U. D. C. 543.544 : 541.8

Determination of the Thermodynamic Functions of Solutions by Gas-liquid Chromatography

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This review of the latest progress in gas-liquid chromatography is devoted to a description of the methodologi experimental technique for the gas-chromatographic determination of the thermodynamic properties of soluti are given for the calculation of the chief thermodynamic functions—the distribution constant, activity coeffi entropy, and free energy of the solution. The bibliography contains 152 references.

CONTENTS

I. Introduction 174
II. Classification of chromatographic methods for determining the thermodynamic properties of solutions 174
III. Calculation of distribution constants from retention volumes 175
IV. Experimental determination of retention data for the calculation of the thermodynamic properties of solutions 177
V. Calculation of activity coefficients 178
VI. Determination of the thermodynamic properties of solutions with medium and high concentrations 180
VII. Calculation of the molar heat of dissolution 181
VIII. Calculation of the molar entropy of dissolution 183
IX. Calculation of the molar free energy of solution 183
Appendix

I. INTRODUCTION

The method of gas-liquid chromatography (GLC), discovered in 1952 by Martin and Synge, has been widely accepted as a means of analysing complex mixtures of substances[1-3]. Although in their first paper the discoverers of the method pointed out not only its possible analytical applications but also methods for studying the physicochemical properties of substances, the application of GLC in physical chemistry has been extremely limited. Since 1955, papers on the study of the properties of solutions using gas-chromatographic methods have been published[4], but up to the present the number of such papers has been measured in tens (the number of papers on the analytical applications of gas chromatography is more than 14 000), although the potential promise of the GLC method for making physicochemical measurements have been pointed out in a number of reviews[5,6].

In GLC, the components of a mixture are separated as a consequence of their different solubilities in the stationary liquid phase, so that it is quite natural to use this method primarily for the study of the resulting dilute solutions of a volatile solute in a non-volatile solvent (coefficients of mass transfer and diffusion, the thermodynamic functions of the solutions, etc.). GLC provides a unique method for the experimental study of the properties of infinitely dilute solutions of volatile substances in non-volatile solvents; a convenient and rapid method for determining the equilibrium composition of solutions is obtained if the components are analysed by gas chromatography. The measurement of solubility by a static method requires several days if the results are to be obtained over a given temperature range, whereas when GLC is used, these measurements can be made in 40–60 min. Before the development of the GLC method, there were only about ten pieces of data characterising quantitatively the solubility of volatile substances in non-volatile solvents at infinitely low concentrations of the solution; now, by means of GLC, such data are numbered in thousands.

II. CLASSIFICATION OF CHROMATOGRAPHIC METHODS FOR DETERMINING THE THERMODYNAMIC PROPERTIES OF SOLUTIONS

All chromatographic methods for determining the thermodynamic functions of solutions can be divided into three groups.

1. Determination of Solubility in a Chromatographic Column by the Development Method

In this instance a study is made of the properties of the solution formed when the solute is passed through a chromatographic column filled with a solid carrier on which is deposited the stationary liquid phase (solvent). The solute is introduced at the start of the chromatographic column in the form of vapour or liquid, and is moved along the column by a stream of carrier gas. Along the column, equilibrium is established between the concentrations of solute in the gaseous and liquid phases. The method of development gas chromatography is suitable for the study of the solubility of volatile substances in non-volatile solvents at low concentrations of the solutions (not greater than 1%) and is technically simple; however careful account must be taken of the experimental conditions. The Henry coefficient should not change with change in the concentration of the solution. The time required for the measurements and their subsequent analysis is not great.

2. Methods Using Frontal Chromatography

These methods are applicable in the study of the thermodynamic properties of solutions at any concentration. They include vacancy chromatographic methods for studying the thermodynamics of solutions. The values of the solubility at different solute concentrations are determined from the parameters of the sorption or desorption wave in the frontal method. In one experiment it is possible to obtain data on the solubility of one component at any concentration of the solution, but the calculation of the thermodynamic quantities from the parameters of the experiment requires some time and skill.

3. Methods in which the Chromatograph is Used as an Instrument for the Quantitative Analysis of the Composition of an Equilibrium Mixture

An advantage of these methods over classical static methods is the small volume of the equilibrium systems studied, since a specimen weighing less than 0.01 mg is sufficient for analysis by gas chromatography. The removal of such a small specimen produces almost no displacement of equilibrium in the system, and the decreased volume of the saturator in which the system being studied is placed facilitates the attainment of equilibrium between the phases in a shorter time. The time required to obtain the experimental data by these methods is greater than the time required for determination by the methods of the first group, but here there are no restrictions on the concentration of the solution and the volatility of the components of the mixture.

A necessary condition for carrying out an experiment by the third group of methods is that it be possible to analyse one or more of the components of the given mixture by gas chromatography. In principle, gas chromatography can be used to analyse any system, the components of which boil without decomposition at any temperature at a pressure of not less than 0.1 torr. Pyrolytic gas chromatography also makes it possible to analyse solid compounds which decompose when distillation is attempted. The apparatus required for methods of the third group is extremely simple for pressures equal to atmospheric pressures; higher or lower pressures require special attachments for the removal of the specimen.

The methods of the second group are used chiefly for the study of two-component systems, whereas this restriction does not apply to the methods in the other groups. An important advantage of chromatographic methods for studying equilibrium is the decreased requirements as to purity of the components of the solution. In the study of equilibrium by the static method from the vapour pressure, any impurities distort the experimental results, whereas gas chromatography makes it possible to determine each component of the solution with a high degree of selectivity. Moreover, if the solution contains several components, their simultaneous determination is always possible in principle, and this increases considerably the efficiency of chromatographic methods of studying solutions. For example, the chromatographic method makes it possible to study equilibria in systems containing up to 20–30 components.

The high sensitivity of gas-chromatographic instruments makes it possible to analyse extremely dilute solutions down to concentrations of $10^{-3}-10^{-4}$%, and hence to obtain valuable experimental data for the development of the theory of infinitely dilute solutions, where it is possible to neglect concentration effects in solubility.

Thus gas chromatography not only makes it possible to obtain thermodynamic data on the properties of solutions with minimal effort but also in a number of instances provides a unique method for determining solubility in infinitely dilute solutions.

III. CALCULATION OF DISTRIBUTION CONSTANTS FROM RETENTION VOLUMES

We can consider the determination of this thermodynamic quantity using the first group of methods, that is in a chromatographic column. When the component being separated moves along a layer of sorbent, thermodynamic equilibrium is effectively established between the liquid and gaseous phases, since as a consequence of the extensively developed surface of the solid carrier the thickness of the film of stationary phase is negligibly small.

The ratio of the quantities of solute in unit volume of the liquid and gaseous phases is defined as the chromatographic distribution constant K:[6]

$$K = \frac{n_l/v_l}{n_g/v_g}, \tag{1}$$

where n_l, n_g, v_l, and v_g represent respectively the number of moles of solute in the liquid and gaseous phases and the volumes of liquid and gas in the chromatographic column.

Subsequently, for the sake of brevity, the chromatographic distribution constant will be referred to as the distribution constant. We can examine how this quantity is related to the characteristics of a sufficiently small section of the chromatographic column, in which the pressure drop of the carrier-gas approaches zero, and the average pressure is 1 atm. The rate of travel of the solute along a given section of the column (u_1) is given by Eqn. (2),[1] since only that fraction of the substance which is in the gaseous phase can be transported by the carrier gas

$$u_1 = \bar{u}f, \tag{2}$$

where f is the fraction of time for which the substance is in the gaseous phase, and $\bar{u}$ the linear velocity of the carrier gas.

We then have

$$f = \frac{n_g}{n_1}. \tag{3}$$

Combination of Eqns. (1) and (3) gives

$$\frac{n_g}{n_1} = \frac{n_g}{n_g + n_l} = \frac{n_g}{n_g + n_g \cdot Kv_l/v_g} = \frac{v_g}{v_g + Kv_l}. \tag{4}$$

If the linear velocity of the carrier gas is defined as

$$\bar{u} = \frac{u}{v_g/\Delta L},$$

where u is the volume rate of flow of gas and ΔL the length of the section of the column, we have

$$u_1 = \frac{u}{v_g/\Delta L}\frac{v_g}{v_g + Kv_l} = \frac{u\,\Delta L}{v_g + Kv_l}. \tag{5}$$

The retention volume of the solute is defined[1-3] as

$$V_R = \tau_R u, \tag{6}$$

where τ_R is the time for which the component is in the column.

Since

$$\tau_R = \frac{\Delta L}{u_1},$$

we have

$$V_R = \frac{\Delta L}{u_1} u.$$

We thus obtain the fundamental static equation in GLC:

$$V_R = v_g + K v_l. \quad (7)$$

Eqn. (7) can be used only for those systems where the pressure drop of the carrier gas in the chromatographic column can be neglected, and the total pressure in the column is equal to 760 torr. Under real conditions of chromatographic column operation, this is not attained, so that it is necessary to consider the corrections made to the retention volume to take account of the change in the pressure of the carrier gas along the column. We can consider the elution of a component from a column of finite length, divided into equal sections ΔL.[7] For a non-compressible gas we obtain

$$V_r = K \cdot v_l \cdot \Delta L,$$

where $V_r = V_R - v_0$.

If N is the number of parts into which the column is divided, we have

$$\tau_r = \frac{V_l}{N} \sum_{i=0}^{i=N} \frac{K_i}{u_i}, \quad (8)$$

where $V_l = Lv_l$.

From the equation of state for an almost perfect gas

$$p = \frac{n_g \cdot RT}{V} + \frac{RT}{V^2} \sum_{ij} B_{ij} x_i x_j,$$

where x_i and x_j are the mole fractions of the components in the gas, and B_{ij} the second virial coefficients for the components of the system, Everett[8] found that at infinite dilution of the solute in the gaseous phase

$$\tilde{v}_g = \frac{RT}{p} + B_{33}, \quad (9)$$

where $\tilde{v}_g$ is the molar volume of the gaseous phase, and B_{33} the second virial coefficient of the pure gas.

We can thus write the following expression for the distribution constant

$$K = \lim_{x_l \to 0} \left\{ \frac{x_l n_l}{x_g V_l} \left[\frac{RT}{p} + B_{33} \right] \right\}. \quad (10)$$

Everett also showed that at a pressure at the inlet to the chromatographic column $p_i < 20$ atm and a ratio $p_i/p_0 < 5$ (p_0 is the pressure at the outlet from the chromatographic column) it is possible, with sufficient accuracy, to write

$$V_R = KV_l [1 + \beta p_0 J_3^4], \quad (11)$$

where

$$J_3^4 = \frac{3}{4} \frac{(p_i/p_0)^4 - 1}{(p_i/p_0)^3 - 1},$$

$$\beta = \frac{2B_{13} - \tilde{v}_1^{\infty}}{RT},$$

B_{13} is the second virial coefficient taking account of the interaction between the solute and the carrier gas, and $\tilde{v}_1^{\infty}$ the partial molar volume of the solute at infinite dilution.

For an ideal gas, the pressure at each point of the column (p) is given by the equation

$$p = \sqrt{p_i^2 - \frac{l}{L}(p_i^2 - p_0^2)}, \quad (12)$$

where l is the distance from the column inlet to the given point.

If however the gas does not obey the laws for ideal systems, it is necessary to take account of the corrections involving the virial coefficient B_{33}:[8]

$$p = \left[p_i^2 - \frac{l}{L}(p_i^4 - p_0^2) - \frac{2B_{33}}{3RT} \left\{ \frac{p_i^3 - p^3}{p_i^2 - p_0^2} + \frac{p_i^3 - p_0^3}{p_i^2 - p_0^2}(p_i^2 - p^2) \right\} \right]^{1/2}$$

$$u = \frac{p_0 u_0}{p} \left[1 - \frac{B_{33}(p_0 - p)}{RT} \right].$$

Overall allowance for the change in the distribution constant with the carrier gas pressure, the effect of the viscosity of the gas, and its effective pressure, makes it possible to write the following equation[7]:

$$V_r = \frac{\frac{KV_l J_3^4}{p_0} \left[\frac{e^{l\beta p}}{\beta^2} \left(\beta^2 p^2 - 2\beta p + 2 \right) \right]_{p_l}^{p_0}}{0.5\,[p^2]_{p_l}^{p}}. \quad (13)$$

From this equation, using the experimentally determined values of the retention volumes of the solutes studied, it is possible to determine the chromatographic distribution constant under standard conditions and the magnitude of the second virial coefficient B_{13}. Eqn. (13) is usually solved graphically, but for analytical calculations an approximate version of this equation is usually employed[9]:

$$\ln V_R = \ln KV_l + \beta p_0 J_3^4. \quad (14)$$

For systems where the carrier gas dissolves in the stationary phase, this effect was taken into account[10] using the derived overall equation

$$\ln V_r = \ln KV_l + \beta' p_0 J_3^4 + \zeta (p_0 J_3^4)^2, \quad (15)$$

where

$$\beta' = \beta + \lambda \left[1 - \frac{\partial \ln \gamma_1^{\infty}}{\partial x_3} \right],$$

$$\zeta = \frac{3C_{133} - 4B_{13}B_{33}}{2RT} + \varphi \left[1 - \frac{\partial \ln \gamma_1^{\infty}}{\partial x_3} \right] + \frac{\lambda^2}{2} \left[1 - \frac{\partial^2 \ln \gamma_1^{\infty}}{\partial x_3^2} \right] + \frac{KV_l}{RT}.$$

The quantities λ and φ characterise the solubility of the gas in the stationary phase. In the expression for ζ the penultimate term characterises the compressibility of the stationary phase. For most systems, however, particularly if the work is carried out at temperatures up to 100°C with common carrier gases, the influence of the solubility of the carrier gas in the stationary phase on the retention volume can be neglected. A number of experiments specially carried out to study the influence of the nature of the carrier gas on the distribution constant[11-15] showed that the solubility of the carrier gas in the liquid need be taken into account only for gases such as carbon dioxide, ethane, and the heavier hydrocarbons.

Thus theoretical allowance for the various possible effects of the experimental conditions on the magnitude of the distribution constant being calculated shows that for its sufficiently accurate determination from a chromatographic experiment, the following data are required: the retention volume V_r, the volume of the stationary phase in the column, and the pressure at the inlet and outlet of the column; to introduce corrections for the non-ideal nature of the gaseous phase in the column it is necessary to take account of the molar volume of the solute at infinite dilution and the second virial coefficient. The last two corrections are rarely used, chiefly to obtain results with an extremely high accuracy, of about 0.5%. In order to introduce the minimal number of corrections in the calculation of the distribution constant from chromatographic data, it is recommended that the studies be carried out with very short columns and a solid carrier with large particle size, to ensure the minimum pressure drop along the column.

IV. EXPERIMENTAL DETERMINATION OF RETENTION DATA FOR THE CALCULATION OF THE THERMODYNAMIC PROPERTIES OF SOLUTIONS

To obtain the true values of the distribution constant, characterising the gas–liquid equilibrium, it is necessary to observe certain precautions, dictated by the nature of the processes occurring in the chromatographic column during the movement of the zone of solute.

For solutions with low concentrations the retention data of a component are independent of the presence of other compounds in the mixture, with the condition that the components of the mixture do not react with one another. Thus it has been shown[16] that in a mixture of benzene, cyclohexane, and methylcyclohexane, no mutual influence of the components of the solution on their retention volumes is observed. The interaction of solutes is observed experimentally only at solute concentrations which are so high that the solution must be regarded as a mixture of components in approximately equal concentrations. When a mixture of substances is introduced into the inlet section of a chromatographic column, all the components of the mixture move in a single zone only in the first sections of the column, after which they separate into zones containing only binary solutions. Thus the mutual influence of the components in a mixture on their retention times is shown most strongly for those substances for which the rates of movement of the zones along the column are similar. In general it is better to carry out the solubility determination with specimens of individual substances or substances with markedly different solubilities.

The stationary phase is applied to the surface of the solid carrier in a very thin film. There naturally arises doubt as to whether the nature of the dissolution is the same in these thin layers in the chromatographic column and in static experiments. The vapour pressure above a pure liquid and a layer of liquid deposited on a chromatographic carrier of the celite type has been measured[17–19] and it has been shown that the results of the static and chromatographic experiments are identical. These conclusions are applicable for fairly large quantities of stationary phase on the carrier—more than 0.03 volumes of liquid per volume of solid carrier.

The stationary phase is present on the surface of the solid carrier in two energetically different states—as an absorption layer and as capillary liquid[20]. The adsorption layer of liquid has a low entropy of solution compared with the pure liquid, whereas the properties of the capillary liquid and the pure liquid are identical. With small quantities of stationary phase on the carrier, due to the effect of the adsorption layer of liquid, the solvent power of the stationary phase is lower than that of the pure liquid[21]. With increase in the quantity of stationary phase on the carrier, the solubility increases exponentially, since the relative quantity of capillary liquid in the stationary phase increases.

When a solute passes through a chromatographic column, the maximum concentration in the solution in the zone decreases, as a consequence of spreading by diffusion[1]. If the experiment is carried out under conditions where the concentration in solution in the first sections of the column is extremely high, concentration distortion of the value of the distribution constant is observed. To decrease the influence of concentration effects it is desirable to use columns with a large quantity of stationary phase on the carrier.

The size of the specimen placed on the chromatographic column also influences the concentration of the gas-chromatographic solution. It is desirable to have a specimen which is sufficiently small, at the concentrations of the solutions formed in the stationary phase, for the values of the distribution constant to remain constant, that is for Henry's law to apply. At a ratio of the quantities of stationary phase and carrier greater than 0.01 : 1, an activity coefficient in the range 0.5–1.5, and size of specimen up to 2 μmole (column with internal diameter 4 mm), distortions of the experimentally observed values of the distribution constants were not observed for non-polar systems[17].

As the chromatographic zone moves along a column, processes of condensation and volatilisation lead to a change in the temperature of the solution. It was calculated[17] that these micro-changes in temperature under the real conditions indicated above do not exceed 0.1 deg, and this has almost no influence on the experimentally determined retention data.

When a solute passes through a chromatographic column the viscosity of the carrier gas changes as a consequence of the formation of a gaseous zone of mixed solute and carrier gas, and this produces pressure surges along the column. According to published data[5], these surges are negligibly small if the specimen size is less than 1 μmole, the activity coefficients between 0.2 and 5, and the retention volume of the solute, corrected for the dead volume, not less than 500 ml. It has been shown[17,22] that the nature of the carrier gas has no influence on the magnitude of the distribution constant (the following gases were studied: helium, hydrogen, nitrogen, oxygen, argon, carbon dioxide, and methane). On the other hand, results obtained by capillary chromatography show that the retention data depend on the nature of the carrier gas[23], although it is possible that with the large pressure drops encountered in capillary columns, the authors cited were unable to calculate the distribution constant with sufficient accuracy.

As the chromatographic zone passes through the column, its rate of movement depends on three factors: the solubility in the stationary phase (K), the adsorption at the gas–liquid interface, and the adsorption at the solid–liquid interface[24–27]:

$$V_r = Kv_l + K_{gl}s_l + K_{ls}s_s, \qquad (16)$$

where s_l and s_s represent respectively the surface areas of the liquid and solid in the chromatographic column, and K_{gl} and K_{ls} the adsorption coefficients at the gas–liquid and solid–liquid interfaces respectively. These phenomena were first observed for systems formed by a non-polar solute and a polar solvent[25,28].

To calculate the constant of this equation it is necessary to determine experimentally the dependence of the retention volume on the quantity of stationary phase in the column and the surface area of the stationary phase. The calculations are then carried out by means of the equations[27,29]:

$$\frac{V_r - \bar{V}_r}{v_l - \bar{v}_l} = K + \frac{s_l - \bar{s}_s}{v_l - \bar{v}_l}, \qquad (17)$$

$$\frac{V_r - \bar{V}_r}{m - \bar{m}} = V_g + K_{gl}\frac{s_l - \bar{s}_l}{m - \bar{m}}, \qquad (18)$$

where $\bar{V}_r$ is a selected value of the retention volume for the sorbent, characterised by the quantities $\bar{m}$ and $\bar{s}$, and V_g the specific retention volume.

Eqns. (16)–(18) are applicable for sufficiently large quantities of stationary phase on the carrier—greater than 1% of the weight of sorbent. The characteristics of adsorption at the boundaries between the phases in GLC have been calculated by a number of authors[24–30].

The adsorption of solutes on the surface of the stationary phase is most marked in the chromatography of non-polar substances on a polar stationary phase, but even when a non-polar stationary phase is used, allowance must be made for this effect[30].

A number of authors[29,31-36] have made detailed studies of the effects associated with the adsorption of a solute at the interface between the solid and the stationary liquid phase. These effects are least marked when the gas-chromatographic method is used to study non-polar systems. Polar solutes are usually readily sorbed by the surface of the diatomites used as carrier in GLC. This leads to a change in the retention time with the size of the specimen, and the effect is greatest with small quantities of stationary phase on the carrier[37,38]. Particular care in the thermodynamic treatment of chromatographic data is required for solutions of polar substances in non-polar solvents, where various concentration distortions can affect the determination of retention volumes[39]. Polar stationary phases to some extent modify the carrier surface, decreasing its adsorption activity with respect to polar compounds. The best results in decreasing the adsorption power of the carrier surface are achieved by treating the diatomites with silane; it is always best to do this when non-polar stationary phases are used. In some instances, satisfactory results have been obtained on solid carriers with a non-polar surface—Teflon[30] or polyethylene[40]. Interfacial adsorption produces particularly marked distortion of retention volume values in those instances where the substances being separated have small distribution constants. For $K > 100$ and correctly chosen experimental conditions, the fraction of interphase adsorption does not exceed 2–3% of the total retention volume[26,28].

When the first portions of stationary phase are deposited on a solid carrier, an adsorption layer of liquid is formed; the total surface area of the liquid increases until the solid carrier is completely covered. With further addition of liquid, the pores of the carrier are filled, so that the total surface area of liquid decreases exponentially towards a limiting value. The addition of liquid also increases the concentration of capillary liquid in the stationary phase, so that the total solvent power of the stationary phase increases. As a result, the curve giving the dependence of the distribution constant, calculated with allowance for adsorption at the solid–liquid interface, on the quantity of stationary phase on the carrier shows a maximum for very small quantities of stationary phase, and a minimum when the volume of staionary phase is about 2% of that of the diatomite carrier[21]. At ratios of stationary phase to solid carrier greater than 0.03 : 1, the values of the distribution constant are stabilised. The heats of dissolution remain constant for proportions of stationary phase greater than 0.01 : 1.

In general, it is best to use capillary columns to obtain information on the thermodynamics of solutions. Thus in the determination of retention data for polar compounds in non-polar stationary phases[41], marked discrepancies were observed between the results obtained on packed and capillary columns. For polar stationary phases, the retention characteristics are similar for the two types of column. The calculation of the specific retention volume of *n*-heptane in squalane on a capillary column[27] gave the values 1550 ml g^{-1} without allowance for interphase adsorption, and 416 ml g^{-1} after the necessary corrections. Littlewood[42] used packed micro-columns with a small quantity of stationary phase on a solid carrier, and this was the main reason for the difference between the experimental results and static data. Martire and Pollara[43] calculated the retention volume not from the apex of the peak, as is usually done in GLC, but from the start of the emergence of the peak, which explains the distortion of the results.

A correctly chosen procedure for the determination of the thermodynamic functions of solutions from gas-chromatographic data makes it possible to obtain reliable values for the distribution constants, agreeing with the results of static experiments[17,44-48]. According to these results, the discrepancy between the results obtained by gas-chromatographic and static methods did not exceed 1%.

To obtain precise experimental data on the thermodynamics of solutions it is necessary to take account of all the parameters of the gas-chromatographic process appearing in Eqn. (14). The procedure has been described in sufficient detail by a number of authors[16,49,50]. For the experiment, the substance being studied is introduced into the chromatographic column in the form of liquid or vapour, and the time taken for the apex of the peak for the component to emerge is measured with a stopwatch. The time correspond to the emergence of the peak for air or methane (τ_0) is then subtracted from the measured time, the carrier gas flow rate is measured with a bubble flowmeter, and all the other necessary parameters of the process are noted. The total time taken for the experiment is usually not more than half an hour per component. Use of the correct experimental procedure in the gas-chromatographic method makes it possible to obtain thermodynamic values of the distribution constant with a small error of the order of 1%.[22] In some instances this error has been halved[17,51]. A number of structural changes in chromatographic instruments, particularly improved methods for controlling the carrier gas flow, made it possible to achieve an accuracy of the order of 0.2% in the determination of the specific retention volume[52,53] or 0.02% in the calculation of the relative retention volume[54]. In the work cited[54], a chromatograph with automatically controlled carrier gas flow rate was used. When it is remembered that the results refer to solutions at limiting dilution, it is clear that such high experimental accuracy cannot be achieved by any other method.

High accuracy in the determination of solubility characteristics by GLC is realised only for components present in the mixture in medium concentrations. In the study of retention data for substances with a high concentration in the mixture it is necessary to introduce a number of corrections[55]. It has been found[56] that with change in the concentration of a trace component from 0.03% to 2% the value of the retention volume of this component changes by 2–3%.

V. CALCULATION OF ACTIVITY COEFFICIENTS

Thus experimental retention data obtained by development GLC can be used to calculate the chromatographic distribution constant K. For more universal application of this parameter it is necessary to relate it to the thermodynamic distribution constant $\bar{K}$, given by the equation

$$\bar{K} = a_l/a_g, \qquad (19)$$

where a is the activity, equal to γc (γ is the activity coefficient†, and c the concentration).

† In GLC, the standard state of the solute in the calculation of the activity coefficient is usually taken as the pure solute under normal conditions, so that for infinitely dilute solutions $\gamma \neq 1$. The quantity γ shows the departure of the solute vapour pressure from the value which would be observed for an ideal solution.

Warnings against confusion of the thermodynamic and chromatographic distribution constants have been published[57,58]. In the latter work the following relationship was derived for converting the chromatographic distribution constant into the thermodynamic constant:

$$\overline{K} = \frac{c_l/n_l}{pc_g/n_g} = \frac{K}{N_l RT} \qquad (20)$$

N_l is the number of moles per unit volume of the stationary phase. From this we can readily calculate the molar free energy of dissolution

$$\Delta G_s = -RT \ln \overline{K}. \qquad (21)$$

We can establish the relationship between the distribution constant and the activity coefficient for dilute solutions[6,59,60]. For non-ideal solutions, Raoult's law is written as

$$yp = \gamma_p^{\infty} x p^0,$$

where x and y represent respectively the mole fractions of the solute in the liquid and solid phases.

Since

$$K = \frac{xN_l}{yN_g} = \frac{xpN_l}{\gamma_p^{\infty} x p^0 N_g}$$

and

$$p/N_g = RT,$$

we obtain

$$\gamma_p^{\infty} = \frac{N_l RT}{Kp^0}. \qquad (22)$$

To take account of the non-ideal nature of the gaseous phase, we can use the equation derived by Everett[8] making the same assumptions as when correcting the distribution constant

$$\ln \gamma^{\infty} = \ln \frac{N_l RT}{Kp^0} - \frac{(B_{11} - \tilde{v}_1^0)p^0}{RT} + \frac{(2B_{13} - \tilde{v}_1^{\infty})p}{RT}, \qquad (23)$$

where $\tilde{v}_1^0$ is the partial molar volume of the solute, and p^0 the vapour pressure of the solute at the temperature of the experiment.

A similar type of equation was derived by Cruickshank and coworkers[9]. The chief difference between Eqns. (22) and (23) is that in the former, the activity coefficient is calculated with the assumption that the gaseous phase is non-ideal, and the vapour pressure of the pure solvent obeys the laws for ideal gases; the second equation takes account of all the deviations from ideal behaviour which can arise in a chromatographic experiment. Thus Eqn. (23) gives a more accurate value for the activity coefficient.

If data on the fugacity of the substance being studied are available, the activity coefficient is calculated from the equation

$$\gamma^{\infty} = \frac{N_l RT}{Kf^0}, \qquad (24)$$

where f^0 is the fugacity of the vapour of the pure solute at the temperature of the experiment.

A somewhat inconvenient feature of the above equations is the need to determine the density of the stationary phase (solvent) at all temperatures of the experiment, since the volume of the stationary phase appears in the equation for the calculation of the chromatographic distribution constant. It is therefore preferable to use the specific retention volume (V_g), where the retention volume of the component is related to unit mass of the stationary phase in the column. The last quantity is independent of temperature:

$$V_g = \frac{273.2 \cdot V_r}{m \cdot T}, \qquad (25)$$

where m is the quantity of stationary phase in the column, g. The retention volume in Eqn. (25) is also corrected for the non-ideal nature of the gaseous phase, as with the distribution constant. The activity coefficient is calculated with allowance for the specific retention volume by means of the equation

$$\gamma^{\infty} = \frac{273.2R}{MV_g f^0}. \qquad (26)$$

In estimating the selectivity of the stationary phase in gas-liquid chromatography, considerable use has been made of relative values of the activity coefficients, for which some readily available compound is taken as standard (for example benzene, carbon tetrachloride, n-alkanes). The relative activity coefficient is calculated from the minimum in the experimental data

$$\gamma_{xr}^0 = \gamma_x/\gamma_r = \frac{f_r^2}{f_x^0 V_r^0} = 1/f_{xr}^{00} V_r^0, \qquad (27)$$

where v_r^0 is the relative retention volume, and f_{xr}^{00} the relative volatility of the substances being compared.

If the activity coefficients of a large number of compounds are being determined, it is usual, for convenience, to choose one of them as standard and to calculate relative values of the activity coefficients for the others. The absolute value of the activity coefficient is measured for the standard component. The accuracy of the determination of the relative activity is then greatest, and reaches 0.05%, indicating that the extensive use of the relative values is appropriate.

GLC provides the experimentalist with extensive possibilities for studying systems with multicomponent solvents[61]. The composition of the stationary phase in the chromatographic column may be altered arbitrarily. In such instances it is necessary to make allowance for purely gas-chromatographic effects associated with the use of small quantities of added polar substances, which may be sorbed by the surface of the solid carrier and hence influence not so much the solubility of the substances in the mixed stationary phase as the degree of chemical modification of the surface of the solid carrier[49].

If the stationary phase volatilises from the column under the conditions of the experiment, it is possible in the measurements to weigh the column before and after the experiment in order to make allowance for the loss of liquid and to make a corresponding correction to the retention data[62,63]. In a number of experiments[6,48,64] with volatile stationary phases, use has been made of saturators placed in front of the chromatographic column. The saturator contains solid carrier, impregnated with a large quantity of the stationary phase. Carrier gas at the temperature of the column passes through the saturator and is saturated by the vapour of the stationary phase. The loss of stationary phase from the column is compensated by the introduction of fresh portions of material from the saturator. This method has two important advantages over weighing the column before and after the experiment; firstly, the quantity of stationary phase remains unchanged during the experiment, and secondly, the stationary phase is distributed uniformly along the entire length of the column, whereas when the method of weighing is used, the liquid volatilises primarily from the start of the column. This last feature may lead to marked distortion of the results, due to the marked concentration dependence at

the low concentration of stationary phase in the first sections of the column.

The activity coefficients in systems containing benzene, toluene, *n*-propanol, dichloroethane, and carbon tetrachloride have been determined[50]. Allowance was made for the non-ideal nature of the gaseous phase, resulting from the presence of the vapour of the volatile solvent.

The use of circulation arrangements also makes it possible to carry out the determinations in systems with a volatile stationary phase. For example, the activity coefficients of methanol and ethanol (solvent benzene) were determined at 25° on a circulation apparatus[65].

Methods for the determination of activity coefficients by GLC have been reviewed[66], and the influence of departure of the behaviour of the gaseous phase from ideal behaviour on the values of the thermodynamic quantities has been discussed[67].

VI. DETERMINATION OF THE THERMODYNAMIC PROPERTIES OF SOLUTIONS WITH MEDIUM AND HIGH CONCENTRATIONS

The above material relates to the determination of thermodynamic data at infinite dilution, that is in the very dilute solutions existing in the chromatographic column. For the theory and practical utilisation of solutions it is of interest to study solutions of substances at finite concentrations. Static methods for obtaining these results require considerable expenditure of effort and complicated experimental technique[68,69]; the chromatographic method is free from these disadvantages.

A method for determining solubility over a wide range of solution concentrations by frontal gas chromatography has been described[70]. A stream of carrier gas passes through an ordinary gas-chromatographic assembly, the column of which contains a measured quantity of stationary phase on a solid carrier. At a selected moment, the stream of carrier gas is passed through a saturator containing the solute. The temperature of the saturator is chosen to create the required vapour pressure of solute in the carrier gas. The chromatograph records the appearance of a concentration wave at the outlet from the column. When the concentrations of the substance added to the carrier gas have become the same at the inlet and outlet, pure carrier gas is passed through the column, and the chromatograph records the desorption concentration wave. The assembly is calibrated with respect to the concentration of the saturated vapour of the substance being studied in the carrier gas. The solubility is calculated from an arbitrarily selected number of points on the sorption or desorption curve. The quantity of substance sorbed is calculated from the equation

$$q = \frac{cV - q_1}{m}, \qquad (28)$$

where q_1 is the quantity of substance eluted from the column at the moment of emergence of the point of the curve corresponding to the concentration c, and v the volume of carrier gas which has left the column up to the moment when the concentration c of solute appears at its outlet.

The quantity of substance which has left the column (q_1) is determined directly from the chromatogram by planimetry. This method makes it possible to determine the distribution constants over a wide range of concentrations in one experiment.

A similar method for determining solubility by frontal chromatography was described by Condér and Purnell[71], but in this instance allowance was made for the non-ideal nature of the gaseous phase. An equation was derived[71-73] for determining the activity coefficient at finite concentrations of the solution

$$\ln\gamma = \ln\frac{RT(c_l v_l + n_l)}{p^0 K v_1} + \frac{p_0 J_3^4}{RT}[2xB_{11}J_3^4 + 2(1 - xJ_3^4)B_{13} - \tilde{v}_1^0] - p^0/RT\,[B_{33} - \tilde{v}_1], \qquad (29)$$

where n_1 is the total number of molecules of solvent in the column, and $\tilde{v}_1^0$ the partial molar volume of the solute.

The determination of the distribution constants at finite concentrations of the solutions from chromatographic data is based on the equation[71]

$$V_R = V_0 + m(1 - J_3^4 x)\partial q/\partial c. \qquad (30)$$

In practical measurements, the stream of carrier gas, saturated with the vapour of the component being studied at a definite concentration, is passed through a short column with a small pressure drop. Thus an equilibrium mixture of carrier gas and solute is passed constantly through the column, and the concentration of the solution in the column is known and constant along the entire length of the column. A small specimen of the substance being studied is introduced into the column; this gives a positive peak on the chromatogram. The retention time of this peak is used to calculate the quantity $\partial q/\partial c$ from Eqn. (30). The work cited gives equations which make it possible to make corrections for the non-ideal nature of the gaseous phase when the frontal method is used.

The methods for determining the thermodynamics of concentrated solutions, described in the works cited[70,71], differ in the time taken for the experiment. In the first, the experiment takes a comparatively short time compared with the time required for the calculation of the distribution constants. In the second method, the experiment takes more time than the calculations. The time required for the determination of the solubility isotherm by means of a McBain balance is approximately the same as that for the chromatographic method, if the solvent in the static method is deposited on a solid carrier of the diatomic type. If however the static experiment is carried out with pure liquid, the time taken for the determination of the dissolution isotherm is not less than 3 d. The chromatographic determination and calculations take 3–6 h.

The accuracies of the chromatographic and static methods for determining the solubility in concentrated solutions have been compared[17,71,74]. It has been shown that when a McBain balance is used in a purely static experiment the error in the determination of the activity coefficient is 0.1% at a mole fraction of the solute $x = 0.4$, and 0.4% at $x = 0.2$. If in the static determinations the solvent is deposited on a solid carrier[18], however, the error is 1.5% at $x = 0.4$, and 4% at $x = 0.2$. The error obtained when chromatographic methods are used to determine the distribution constants in these systems is not greater than 0.2%.[71] Thus for the same expenditure of time on the experiments and the treatment of the results, the accuracy of the static method is much less than that of the chromatographic method; for equal accuracies in the determination, the measurement of solubility by the static method requires much more time.

Some authors[75-78] have proposed a method for determining sorption isotherms from the trailing edge of the chromatographic zone (peak) leaving the column in development chromatography. In actual fact, the form of the peak depends on the sorption isotherm, but this is by no means the only factor influencing the form of the peak.

Various diffusion processes also distort the form of the peak, so that it is extremely difficult to separate the contribution of the sorption isotherm in the formation of the trailing edge of the zone in a real chromatographic experiment. Thus these methods for determining the sorption isotherms are extremely approximate, so that they can be used only in gas-adsorption chromatography for substances with a high adsorption capacity. It is more rational to determine the dependence of the time of emergence of the apex of the chromatographic peak on the height of this peak, that is on the maximal concentration of the component in the chromatographic zone. For these determinations, short columns with a small pressure drop are used, but in these instances account must be taken of the fact that the concentration of the solution changes along the length of the chromatographic column.

An original method for determining solubility (V_g) was proposed by Zhukhovitskii and coworkers [79-83]. These methods are suitable for determining the solubility of substances in solutions at concentrations as high as required. A version of chromatography without carrier gas is used for the determinations; the mixture being studied, with or without an inert gas, is passed through the chromatographic column until equilibrium is established along the entire column. Some perturbation to the flow is then created, or a small specimen of air or any substance being studied is introduced, after which the time of emergence of the peaks, the number of which is smaller by one than the number of components in the gaseous phase, is determined. The retention volume of the component, obtained in this way, is related to the distribution constant by the equation

$$V_g = n_g(\partial q_3/\partial n_3 - \partial q_3/\partial n_g) + n_3(\partial q_1/\partial n_g - \partial q_1/\partial n_3), \qquad (31)$$

where the subscripts 1 and 3 refer respectively to the solute and the diluent gas or second component of the mixture. For multi-component systems, similar equations are compiled and solved on electronic computers.

An experimental assembly for the determination of solubility for solutions with concentrations up to 12% has been described [83]. The required concentration is established by adding a sufficiently large specimen of the substance being studied to a column, and the solubility is determined by vacancy chromatography. The distribution constants and activity coefficients for non-polar systems in the concentration range 0–10% have been determined by vacancy chromatography [84]. Comparison of data obtained by the static and vacancy-chromatographic methods for the *n*-hexane–1,2,4-trichlorobenzene system [83] shows that for solution concentrations $x \leq 0.2$ the results agree satisfactorily, but differences are observed at higher concentrations. An important advantage of vacancy-chromatographic methods over frontal methods is that it is possible to study multi-component systems.

The accurate establishment of the quantity of stationary phase in a chromatographic column presents a difficult experimental problem. The accuracy of the results obtained in a gas-chromatographic experiment depends to a large extent on the solution of this problem. Thus a number of authors have tried to combine the advantages of the static method, where an accurately measured quantity of pure stationary phase (solvent) is used, with the chromatographic determination of the equilibrium composition of the gaseous or liquid phase of the system. The design of an apparatus in which the gaseous phase from the static system passes through heated connections into the inlet compartment of a gas chromatograph has been described [85]. The chromatograph is used to determine quantitatively the concentration of the component being studied in the gaseous phase. This method can be used to study multi-component systems, and the calculation requires little time [85,86]. A slightly different modification of the flow system, in which the carrier gas was saturated with vapour from a solution and passed to the inlet chamber of the chromatograph, has been described [87], but in this instance the calculation of the results is extremely complicated.

For the periodic gas-chromatographic analysis of the phase composition of equilibrium systems it is possible to use saturators of small volume with a thin layer of solvent; this makes it possible to establish thermodynamic equilibrium fairly rapidly in the system [49]. A specimen of the gaseous phase from the saturator at constant temperature is removed with a gas syringe with piston stop or with a special micro-column, and introduced into the inlet chamber of a chromatograph with a flame-ionisation detector. The design of these systems is very simple only when the total pressure in the system is equal to atmospheric; otherwise, special attachments are required for the removal of the specimen. A disadvantage of this method is the appeciable time—about 0.5 h—taken for equilibrium to be established in the system, but the calculation of the results is extremely simple.

An important advantage of combined static–chromatographic methods is that it is possible to study systems in which all the components are volatile at the temperature of the experiment. Thus this method has been used to measure the solubility of inorganic gases in electrolytes [88] and the solubility of organic gases in various solvents [89-92]. In these last experiments, the solvent was added to a vessel containing the gas being studied, after which the gas was blown from the vessel to the inlet chamber of the chromatograph and its concentration was measured.

Comparison of different methods for the chromatographic determination of the thermodynamic functions of solutions shows that at low concentrations it is best to use the purely chromatographic method of determining the distribution constants. When it is necessary to measure the solubility at finite fixed concentrations of the solutions, it is rational to use special frontal development methods and chromatography without carrier gas, and also to combine static and gas-chromatographic methods. The use of gas chromatography makes it possible to study the properties of infinitely dilute solutions, to increase the accuracy of experimental thermodynamic data for dilute solutions, and to save time in experiments in the study of concentrated solutions.

VII. CALCULATION OF THE MOLAR HEAT OF DISSOLUTION

Eqn. (22) can be written in the logarithmic form [59]:

$$\ln K = \ln N_1 RT - \ln\gamma - \ln p^0 \quad .$$

According to the basic principles of thermodynamics

$$RT\ln\gamma = \Delta\bar{H}_s - T\Delta\bar{S}_s$$

(the bar above the symbol for a function denotes that the function is an excess function, i.e. it expresses the difference between a property of the pure substance being studied and the same property of the solution), so that we can write

$$\ln K = \ln N_1 R - \Delta H_s/RT - \Delta\bar{S}_s/R + \Delta H_v/RT - \ln(1/T) \qquad (32)$$

where N_1 is the number of moles in unit volume of the stationary phase, and ΔH_V the molar heat of volatilisation. Differentiating this equation with respect to $1/T$ and multiplying by R, we obtain

$$\Delta H_s = R\partial \ln K/\partial (1/T) - RT + R \ln R\partial \ln N_l/\partial (1/T) . \quad (33)$$

This equation makes it possible to calculate the molar heat of dissolution from the experimentally determined chromatographic distribution constants[4,59]. The need to determine the specific gravity of the solvent at different temperatures of the experiment introduces some inconvenience. This can be avoided by using the specific retention volumes for the calculation of the molar heats of dissolution[93]. According to the definition of the specific retention volume,

$$K = \frac{V_g mT}{273.2 v_l} .$$

Substituting this expression in Eqn. (33) and differentiating with respect to $1/T$, we obtain

$$\Delta H_s = R\partial \ln V_g/\partial (1/T) . \quad (34)$$

This equation shows that there is no need to determine the specific gravity of the stationary phase.

The heats of dissolution can be determined experimentally using activity coefficients. The equation relating the activity coefficient and the excess enthalpy of dissolution can be written

$$\Delta \overline{H}_s/T = -\Delta \overline{S}_s - R \ln \gamma .$$

Differentiation with respect to $1/T$ gives

$$\Delta H_s = R\partial \ln \gamma/\partial (1/T) . \quad (35)$$

Since this last equation contains the activity coefficient, the calculation of which requires data on the volatility of the substances being studied, the use of these equations in physicochemical determinations is limited.

The chromatographic determination of the heat of dissolution can be simplified further by eliminating from the necessary experimental data the mass of liquid in the column. The specific retention volume can be written as

$$V_g = \frac{273.2 u \tau_r}{mT} = k' \frac{\tau_r}{\tau_0 T} .$$

Since $u = k''/\tau_0$,

$$\ln V_g = \ln V_{g1} - \ln V_{g2} = \ln \frac{\tau_{r1}\tau_{02}}{\tau_{r2}\tau_{01}} + \ln \frac{T_1}{T_2}$$

so that

$$\Delta H_s = 4.58 \frac{\lg \frac{\tau_{r1}\tau_{02}}{\tau_{r2}\tau_{01}}}{1/T_1 - 1/T_2} + 4.58 \frac{\lg T_2/T_1}{1/T_1 - 1/T_2} , \quad (36)$$

where τ_0 is the time of emergence of the non-sorbed gas (dead volume of the system) and τ_r the actual time of emergence of the solute.

By selecting from the plot of $\lg \tau_r/\tau_0$ against $1/T$ the temperature range in which $1/T_1 - 1/T_2 = 4.58 \times 10^{-4}$, we obtain the final equation for these conditions:

$$\Delta H_s \cdot 10^4 = \lg \tau_{r1}/\tau_{01} - \lg \tau_{r2}/\tau_{02} + \lg (1 + 4.58 \cdot 10^{-4} T_2) \quad (37)$$

where the heat of dissolution is expressed in calories.

Thus the use of the last equation makes it unnecessary to determine the quantity of stationary phase in the column.

In the calculation of the heat of dissolution, allowance must be made for the difference between the enthalpy and heat of dissolution. The enthalpy of dissolution in most instances is negative, whereas the heat of dissolution has the opposite sign. The heat and enthalpy of dissolution are calculated by means of the same equations, and the quantities differ only in their signs. In most papers on gas chromatography, the heat of dissolution is denoted by H, and this may sometimes lead to confusion between thermodynamic and chromatographic data, since in chemical thermodynamics, heat is denoted by Q, and enthalpy by H.

A quantity used extensively in GLC is the relative heat of dissolution $\Delta H^0_{sx} = \Delta H_{sx} - \Delta H_{st}$, where ΔH_{sx} and ΔH_{st} are respectively the molar heats of dissolution of the substance being studied and a standard substance.

By carrying out the same steps used to derive Eqn. (37), we obtain a working equation for calculating the relative heat of dissolution from the difference in the logarithms of the retention volumes for $\Delta(1/T) = 4.58 \times 10^{-4}$:

$$\Delta H^0_s \cdot 10^4 = \lg V^0_{r1} - \lg V^0_{r2} . \quad (38)$$

It can be seen from Eqn. (38) that the calculation of the relative heat of dissolution from the relative retention volumes requires a minimum of experimental data.

Heats of dissolution can also be determined from data obtained for solutions with different concentrations by frontal, development, vacancy-chromatographic, and static-chromatographic methods. In these instances the isosteric heat of dissolution is usually calculated.

Many workers have determined heats of dissolution experimentally from retention data, and the experimental procedure has been described in detail[49,59,93-97].

Since in GLC practice extensive use is made of the so-called retention index, an attempt was made[98] to calculate the enthalpy of dissolution from the temperature dependence of the retention index

$$\Delta H_s = \frac{\delta I_n}{100} (\Delta H_{sr+1} - \Delta H_{sr}) + \Delta H_{sr} \quad (39)$$

where $\delta I_n = I_1 - IT_1/\Delta T$; $\Delta I = I_1 - I_2$; $\Delta T = T_2 - T_1$; I is the retention index of the substance being studied, and ΔH_{sr} the molar heat of dissolution of the n-alkane with the same number of carbon atoms in the molecule as the substance being studied, and ΔH_{sr+1} the molar heat of dissolution of the n-alkane with one carbon atom more in the molecule than the molecule of the substance being studied. The standard deviation which can be allowed when Eqn. (39) is used to calculate heats of dissolution is about 0.1 kcal mole^{-1}; in some instances, however, the discrepancy between the values of the heats calculated from the retention indices and from the retention volumes can reach 0.4 kcal mole^{-1}.

With precision measurement of the retention volumes, the reproducibility of the experimentally determined relative heats of dissolution is 0.02 kcal mole^{-1}, and that for the absolute heats 0.05 kcal mole^{-1}. Although the values of the heats of dissolution determined chromatographically agree to within an order of magnitude with the calorimetric values, there are as yet no sufficiently accurate calorimetric data on heats of dissolution for infinitely dilute solutions, so that a quantitative comparison of the chromatographic and calorimetric values cannot be made. Thus GLC makes it possible to determine heats of dissolution for solutions with any concentration, including infinitely dilute solutions; this last feature is particularly important.

VIII. CALCULATION OF THE MOLAR ENTROPY OF DISSOLUTION

The excess molar entropy of dissolution is calculated from the equation

$$RT\ln\gamma = \Delta\bar{H}_s - T\Delta\bar{S}_s \ . \qquad (40)$$

On the other hand, we can write the following equation containing the thermodynamic distribution constant:

$$-RT\ln\bar{K} = \Delta H_s - T\Delta S_s \ . \qquad (41)$$

In the last equation, in place of the thermodynamic distribution constant, it is possible to substitute the chromatographic distribution constant or specific retention volume

$$-RT\ln\frac{K}{RTN_1} = \Delta H_s - T\Delta S_s \ . \qquad (42)$$

To calculate the relative molar entropies of dissolution it is necessary to substitute in Eqn. (40) the value of the relative activity coefficient. By expressing the last quantity in terms of the relative retention volume and relative vapour pressure of the pure substances being compared at the temperature of the experiment (p^{00}) we obtain the relationships:

$$-RT\ln p^{00}V_r^0 = \Delta H_s^0 - T\Delta S_s^0 \ ,$$

$$-RT\ln V_r^0 = \Delta H_s^0 - T\Delta S_s^0 \ .$$

The error in the determination of the entropy of dissolution by gas-chromatographic methods is made up of the errors of the determination of the activity coefficient and the heats of dissolution. For relative molar entropies of dissolution the mean error is 0.4 e.u. Examples of the calculation of molar entropies of dissolution can be found in many papers [49,99,100].

IX. CALCULATION OF THE MOLAR FREE ENERGY OF A SOLUTION

This quantity is calculated from classical thermodynamic relationships using the distribution constant or activity coefficient

$$\Delta G = -RT\ln\bar{K} \ , \qquad (44)$$

$$\Delta\bar{G} = -RT\ln\gamma \ . \qquad (45)$$

Finally, a number of points may be made regarding the interpretation of the thermodynamic quantities obtained by gas-chromatographic measurements [57]. In the treatment of data on the thermodynamics of solutions of non-electrolytes, two standard states can be used: the pure solute (the distribution constant in this instance is denoted K_3, and an infinitely dilute solution of the same substance (for this standard state the corresponding symbol is K_2). For the gaseous phase, the standard state is usually taken as the ideal gas at a pressure of 1 atm. In the first instance the activity coefficient shows the departure of the properties of the solution from the ideal: the extent to which the vapour pressure of the solute in the solution is less than or greater than the value which would be observed for an ideal system. In GLC it is this standard state which is used in the calculation of the activity coefficient. The activity coefficient for the second standard state characterises the departure of the properties of the solution from Henry's law. These two standard states lead to different quantitative expressions for the thermodynamic functions of the solutions. Thus if the subscripts 2 and 3 are used to denote the heats and entropies of dissolution obtained from K_2 and K_3, we obtain the relationships:

$$\Delta H_{s3} - \Delta H_{s2} = -RT(Td\ln\rho/dT + 1) \ , \qquad (46)$$

$$\Delta S_{s3} - \Delta S_{s2} = R\ln\frac{M}{\rho TR} - R(Td\ln\rho/dT + 1) \ , \qquad (47)$$

where ρ is the density of the stationary phase. For example, when silicone 702 with M = 530 is used as stationary phase, the difference in the heats of dissolution according to Eqn. (46) is 0.5 kcal mole^{-1}, and the difference in the entropies of dissolution 10 e.u.

List of examples where GLC has been used to determine the thermodynamic functions of solutions.

Solutes	Solvents	Refs.
C_4–C_5 alkanes	Liquid paraffin	97
Iso-alkanes, fluorine-containing compounds	Octadecane	10
C_{4-6} iso-alkanes	Dinonyl phthalate, squalane	17
C_{5-6} alkanes	Squalane	8
C_{5-12} alkanes	C_{18-36} alkanes	101
C_{5-8} alkanes	Alkanes	102
n-Alkanes	Apiezon	99
Alkanes	Solar oil	103
C_5 alkanes	Amides	104
C_5 alkenes	Nitrobenzene, dodecane	105
Aliphatic hydrocarbons	Various	93
Alkenes	Polar liquids	106
C_{2-6} alkenes	Various	107-110
Alkenes	Silver nitrate solutions	111
Methylcyclohexanes	Various	112
Benzene	Polyethylene glycol cresyl ether	96
Benzene	C_{16-28} alkanes	113
Benzene	Polyphenyls	114
Aromatic hydrocarbons	Various	100
Aromatic hydrocarbons	Various	115-120
C_{6-10} aromatic hydrocarbons	Various	121
Aromatic hydrocarbons	*n*-Decanol	122
Aromatic hydrocarbons	Various	123
Hydrocarbons	Dinonyl phthalate	51
Hydrocarbons	*n*-Heptadecane	124
Hydrocarbons: butane, butenes	Furfural, *n*-dodecane	125
Hydrocarbons	Various	94
n-Hexane, cyclohexane, benzene	Various	126
Benzene, cyclohexane, methylcyclohexane	PEG ethers	16
Hydrocarbons	Various	23
Aliphatic hydrocarbons	Aromatic hydrocarbons	127
Hydrocarbons	Various	128
Hydrocarbons	Squalane	129
Hydrocarbons	Phthalates	130
Aromatic amines	2,4,7-Trinitrofluorenone	131
Alcohols	Squalane	132
Furan and its derivatives	Various	133
Halogenated hydrocarbons	Various	134
Halogenated hydrocarbons	Alkanes	135
Nitrogen-containing compounds	Aromatic hydrocarbons	136
Diphenyl methyl phosphates	Various	137
Chloroacetones	Various	138
Organic peroxides	Various	139
Oxygen-containing substances	Alkanes	140
Oxygen, hydrogen	Electrolytes	88
Hydrocarbons, nitrogen-containing substances	Squalane, octadecane, dinonyl phthalate	23
Alkanes, acetone, alcohols	Squalane, polyethylene glycol, water	87
Aromatic hydrocarbons, heterocyclic compounds	2,4,7-Trinitrofluorenone	141
Ditto	Various	142,143
Hydrocarbons, alcohols, ketones	Squalane, didecyl phthalate, triol	144
Benzene, cyclohexane, alcohol	Various	145
Hydrocarbons and other classes of compound	Water	146
Hydrocarbons	Water	147
Dichloroethane, propanol	Benzene, toluene	148
Glycols, aminoethanols	Polyethylene glycol, Apiezon	95
Ethanol, carbon tetrachloride	Dinonyl phthalate	149
Hydrocarbons, oxygen-containing compounds	Hydrocarbons	48
Hydrocarbons, halogenated hydrocarbons	Squalane, polyglycols	150
Review	Various	49,151 152

In a number of instances in gas chromatography, however, two different standard states are used in the same equation. For example, the departure of the properties of the solution from Raoult's law is taken into account by the expression $p_1 = \gamma p^0 x_1$, where p^0 is the vapour pressure of the pure solute. Since $K_2 = x/p$, we have

$$\Delta G_2 = -RT \ln \gamma p^0 .$$

In this equation the activity coefficient has the standard state corresponding to K_3, and the free energy that corresponding to K_2. Allowance must be made for the fact that in the determination of the chromatographic values of the distribution constants and specific retention volumes, an infinitely dilute solution is taken as standard state. From this it is clear that, for example, the values of the heats of dissolution obtained from the temperature dependence of the specific retention volumes and activity coefficients may differ. In the calculation of the entropy of solutions it is preferable to use an equation containing the distribution constant or the specific retention volume, if the heat of dissolution is calculated from these quantities. In a number of instances, change in the standard state has little influence on the numerical values of the quantities obtained, but in the treatment of thermodynamic quantities for the study of intermolecular interaction the choice of standard state is extremely important.

Thus examination of gas-chromatographic methods for determining the thermodynamics of solutions shows that these methods can give unique data for infinitely dilute solutions, and for solutions with finite concentrations the experimental data obtained by gas chromatography are distinguished by their high accuracy and by the low expenditure of time in the experiment. In the near future the use of gas-chromatographic methods in the study of solutions will apparently give results as fruitful as those obtained in analytical chemistry.

To conclude we are listing examples of work in which GLC has been used for the determination of the thermodynamic properties of solutions (see Table on p. 183).

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